Utilization of ash from a thermal power plant for ceramic composites

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Abstract: This paper aims to investigate the characteristics of the ashes from Turceni Power Plant (ECT) stored in an external dump in order to identify some ways to reuse it. The ash samples have been analysed in terms of their morphological, mineralogical features and physical-chemical properties including radioactivity. Granulometric composition of the dump ash samples depends on the initial coal grain size and material position as both the surface and depth of the dump, the differential sedimentation of particles depending on their size and sampling depth. The chemical composition of ash from ECT depends on the quality and the composition of lignite, as well as on combustion conditions. Oxide composition analysis (X-ray fluorescence, atomic absorption) indicates that it consists mainly of Al and Si oxides. The ash type is silicoaluminous with a composition close to clay lands, characterized by 45.6\% SiO\textsubscript{2}, 18.8\% Al\textsubscript{2}O\textsubscript{3}. Some other constituents are CaO (10.45\%), MgO (2.40\%), Fe\textsubscript{2}O\textsubscript{3} (8.72\%) and in smaller quantities Na\textsubscript{2}O (0.21\%) and K\textsubscript{2}O (1.44\%). Most of the CaO and MgO are bound in sulphates and mixed oxides with SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}. Preliminary measurements of radioactivity show the existence of $^{226}\text{Rd}$ and $^{232}\text{Th}$, the irradiation on radiation protection being at a level, close but lower than of the health admitted norms. Such comprehensive characterisation helps to find out the appropriate ways of ash recycling, giving also the useful information about the power plant combustion efficiency.

Key-Words: Coal ash, Radioactivity, Ceramics, Glass-ceramics

1. Introduction
In Romania, the energy industry generates yearly great amounts of ash and slag which claims a lot of work for transport and storage by landfill. The impact due to lignite burning in the thermal power plants of South-West Oltenia represents a major environmental and economical concern in this region.
The growing production of ash has long caused on environmental problem with technological and economic effects in the world. Currently, large quantities of ash are used for landfilling which cause negative environmental impacts such as leaching of potentially toxic substances into soils and groundwater. The best way to solve the disposal problem of ash is to decrease the quantity for disposal with utilization of ash in the industry [1]. During technological process of coal combustion in boilers, ash and slag results separately [2]. Ash contains fine particles with diameters less than 0.25 mm (also called fly ash, as is easily driven by wind). It leaves the burning chamber in the same time with the combustion gases, being partially retained and collected in the funnels, which are located under the air preheaters, and in the funnels of the chimney. From the funnels situated under the preheaters, the ash is driven by free fall through large diameter pipes (400 mm or 600 mm) with high slope to the ground level, where it is mixed with water and then is disposed to pumps station for sludge.

Slag consists of particles having size of 0.25 – 1mm or more. The slag resulted from burning lignite of each boiler of 1036 t/h of ECT, is crushed and hydraulically transported, by channels to pumps station. The Bagger pumps stations ensure the transport of the ash and slag hydraulic mixture (1:8.....1:10) and disposal to the deposit no.1, which is located on Cplea Valley at about 1.8 km upstream of Târgu-Jiu – Filiaşi route, on the right side of Jiu River. Currently ash and slag can not find an economic use in Romania, now constituting within the category of nondangerous industrial waste category. However, the diverse chemical, mineralogical and morphological properties of ash offer an opportunity to process it and recover various fractions with particular attributes. A variety of fly ash has been
converted into useful ceramics and glass-ceramics (GCs) by several research groups [1,3,4]. Up to now, the research was mainly oriented towards the production of dense ceramic tiles and GC materials for use as architectural components in buildings.

Fly ash is potentially hazardous nature is primarily due to the toxic metals that it contains (Cadmium, Zinc, Lead, Mercury etc.). Thus, it is necessary for the inertization of fly ashes, to look for new technologies in order to immobilize their dangerous components in glass, glass-ceramic or ceramic materials. The chemical composition of fly ash is typical of a common glassy quaternary system (SiO$_2$–Al$_2$O$_3$–CaO–Fe$_2$O$_3$) and therefore, it is feasible to produce glass materials from coal fly ash. The production of vitreous materials can be an effective route for recycling of fly ash because the high temperature involved in the process leads to the complete destruction of the organic pollutants. Furthermore, heavy metals can be incorporated in the glassy product [3]. The fly ash was introduced into a red firing terracotta composition and the optimum fly ash addition was found to be 5 % at the maximum firing temperature of around 900°C [4]. Very interesting results for mixtures of 60 wt % fly ash and 40 wt % clay, with firing temperatures between 900 and 1200°C in the processing of pressed ceramic products were obtained [5]. The use of fly ash as a raw material in the ceramic field is supported by the large production of ceramics products and the amounts of coal fly ash [6].

Ash and slag resulting from steam power plants require approximately 1.2 ha storage space for every million tonnes. Currently in Romania, a great number of ash and slag dumps exist (108) which cover about 2800 ha, the greatest amount (about 800 ha) being in Gorj County [7]. In the present work ash and slag originating from ECT power plant dump was investigated as a reuse material to produce ceramic materials. In Romania only a small amount is utilized, mainly in the concrete [8] and Portland cement production etc. Addition of 20-34% fly ash of total powder amount is beneficial for the workability and segregation resistance of concrete in fresh state. Typically, glass-ceramics obtained from fly ash have been produced by a combination of melting the fly ash and a one or two stage heat treatment for crystallization, nucleation and crystal growth [9-14]. Coal fly ashes were vitrified by melting them at 1773°C for 5 h without any additives. The properties of the obtained glass and the heat treated glass samples produced from coal fly ash were investigated [15]. This paper aims to investigate the characteristics of the ashes from ECT power plant, stored in external dumps in order to identify some ways to reuse it as ceramic material.

2. Materials and methods

2.1. Physical-chemical analysis

The 14 elementary samples of ash and slag mixture from the deposit no.1. Ceplea Valley of ECT, which represent for our study, the source of “raw material” and called “ash” have been taken, see Fig.1. Of the elementary samples were made four cumulative average samples (A, B, C, D) of 30-40 kg which were prepared for laboratory analyses according to SR ISO 5069-1 and 2:1994.

General physical-chemical characterization of cumulative average samples was focused to establish the limits variation of the basic parameters, as: dimensional distribution of particles (according to SR ISO 1953: 1999-Coals. Grain size analysis), moisture content (according to SR ISO 331:1994-Coals. Total moisture content), bulk density (STAS 5630-73-Coke. Determination of bulk density).

Laboratory tests have been carried out in order to establish the chemical composition of the supplied ash samples. For the determination of chemical composition was used X-Ray Fluorescence (XRF) method according to ASTM E 1621-05 and SR EN ISO 12677:2004. The XRF analysis was performed using an Axios-Panalitical device and the corresponding (IQ+) soft, allowing qualitative and semiquantitative evaluation of the chemical composition. An amount of 0.1 gram of ash is melted in a flux of 6.5 g lithium tetraborate, in a Pt crucible using an induction furnace at temperature 1200°C. Finally, a 32 mm diameter homogeneous lens was obtained and analyzed by using a sequential X-ray spectrometer.

2.2. Radioactivity tests

For the radioactivity analysis, the average ash sample was first dried at 105°C for 48 hours after which it was milled, sieved and placed in special boxes sealed with paraffin, and allowed 30 days for the natural series radionuclides to reach equilibrium. After expiry of the time required and reweighting the sample, it was placed on the detector and measured. Spectrum analysis was performed using the necessary software.

For the determination of radioactivity level of ECT ash sample, for sampling was used a flow meter FH 40 G for measuring the equivalent dose rate of photons. Gamma spectrometric measurements were made with several components such as gamma ray detector (Canberra HPGe type Model BE3820), lead...
2.3. Mineralogical analysis

Mineralogical phase analyzes were performed by X-ray diffraction method with parallel beam - scanning axis 2θ / θ, the bulk samples. It was used a Shimadzu XRD 6000 diffractometer with the radiation generator tube power of 1200 W, respectively using Cu-Kα characteristic radiation (λ = 1.541874 Å). Scanning range (2θ) of goniometry was located between 5° and 80°, with 5°/minute angular speed and 0.02° step.

2.4. TG/ATD analysis

TG/ATD were performed on a Mettler Toledo 851 equipment in the temperature range of 25 – 1200°C, under normal atmosphere (air) and a heating rate of 10°C/min. For making the determination the ash samples were placed in crucibles of high purity aluminium oxide.

2.5. High temperature microscopy analysis

For determinations was used Carl Zeiss Jena equipment, electric resistance furnace equipped with installed power of 1000 W and PtRh22 thermocouple and powered by a stabilized power supply adjustment range of 0-10 A. This provides real-time recording of tested specimen geometry change. Also, using the recorded images during cooling of the sample can be calculated the shrinkage of melts during solidification.

3. Results and discussion

The study reveals the relationship between coal - mineral matter - burning condition - ash, including specific information on the Oltenia lignite basin and combustion characteristics of coal in relation to thermochemical processing conditions. So, the study highlights: relationships between the characteristics and quality of coal and ash, the geological structure of the deposit type and specific purpose, exploitation type, nature of sterile intercalations; the peculiarities of the geological formation of layers in Oltenia lignite basin with variable thickness and many of sterile intercalations, which makes them difficult exploitable and with increased quality variation in time and space, variations leading to difficulties in the grinding and burning operation of in power plants; variations of the different petrographic components depending on the source and granulometric sorts [16]; factors determining the characteristics of ash; chemical composition of ash from mineralogical point of view and trace elements.

3.1. Physical characteristics

Granulometric composition in landfill is influenced by the distance from the guns of discharge and sampling depth. Hydraulic disposal of ash generates differential sedimentation of the particles according to their size. The physical characteristics of moisture, bulk density and grain size composition of the studied ash samples are presented in Table 1.

In terms of basic physical characteristics, the ash can be assimilated to a natural sand aggregate of granular type, except for bulk density, characterized by lower values. The explanation lies in the fact that, in comparison with natural granular aggregate (sand, crushed rock), ash has a high content of anorthit (highlighted by diffractometry), a calcium aluminium silicate with low specific density.

It is important to note that the physical parameters of ashes from power plants fall within very narrow limits of variation of values - almost 5%, significant for the technology use, especially in terms of size composition. Considered, with the probability of 50-70%, as the main component in mixtures for obtaining construction materials using industrial waste, the power plants ash is remarkable, at least in terms of dimensional distribution of grain sizes, rather superior of natural granular aggregates (sand, crushed rock), demonstrating the ability to participate in the mixtures with particle sizes in a wide range (0-5 mm), but with an important amount within the medium and fine-medium class, it is known that areas natural aggregates are scarce see Fig. 2.

For all average samples analyzed, the application of mathematical correlation coefficient was of 95%.

3.2. Chemical composition

The chemical composition of ash from ECT depends on the quality and composition of lignite, as well as on combustion conditions. Oxide composition analysis indicates that it consists mainly of Al and Si oxides. The ash type is silicoaluminous with a composition close to clay lands, characterized by 45.6% SiO₂, 18.8% Al₂O₃. Some other constituents are CaO (10.45%), MgO (2.40%), Fe₂O₃ (8.72%) and in smaller quantities Na₂O (0.21%) and K₂O (1.44%). Most of the CaO and MgO are bound in sulphates and mixed oxides with SiO₂ and Al₂O₃, see Table 2.

In terms of chemical composition of ash from ECT falls within the oxide materials class of calcium aluminium silicates with high iron oxide.
content, being comparable in composition to sandy clay derived from natural deposits situated in mountainous areas surrounding limestone massifs.

3.3. Radioactivity

Preliminary measurements of radioactivity show the existence of $^{226}$Rb and $^{232}$Th, the irradiation on radiation protection being at a level, close but lower than of the health admitted norms. Such comprehensive characterisation helps to find out the appropriate ways of ash recycling, giving also the useful information about the power plant combustion efficiency [17].

The radioactivity level of ECT average ash sample is as follows (Bq/kg):
- Ra-226: 137.4 ± 16.5
- Th-232: 82.9 ± 14.9
- K-40: 520.9 ± 52

The present research highlights a radionuclide content of 2-4 times higher that of standard materials, and a radiation with regard to radiation protection, closer but lower than the allowable level admitted by the Minister of Health. The investigation will be continued and the results will be the subject to another scientifically paper.

3.4. Mineralogical and morphological characteristics

Mineralogical phase analysis carried out by X-ray diffraction method, confirms the results of the chemical composition, highlighting crystalline constituents of the coal ash such as: quartz, anorthit and hematite, see Table 3 and Fig. 3. On Fig. 3. the X-ray diffraction pattern, the blue line was assigned to the coal ash sample (made on average sample A).

3.5. Location of the ashes oxide composition in the ternary system CaO - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$

Taking into account the major oxide components of investigated ashes, the average samples compositions (A, B, C, D) were positioned in the $\text{SiO}_2$- CaO- $\text{Al}_2\text{O}_3$ ternary system as shown in Fig.4.

3.6. Complex thermal analysis

3.6.1. TG/ ATD analysis

TG/DTA diagram for coal ash (average sample A) is given in Fig.5. It might be noticed the structural exothermal effect at 473°C and endothermic effect at 1114 -1205 °C due to the melting of ash.

3.6.2. High temperature microscopy analysis

The real-time recording patterns of geometry change made on coal ash specimen (with average composition) with square section of 4 mm are presented in Fig.6. The ash specimen was sintered at 1140 °C and start to flow at 1160°C and at 1200 °C is melted. This behaviour being in good accordance with TG/DTA results as presented in Fig.5.

4. Conclusion

Chemical properties of ash samples reveal adequate characteristics in comparison with those of the ceramic raw materials usually used in the ceramic industry.

Preliminary measurements of radioactivity show the existence of $^{226}$Rb and $^{232}$Th, the irradiation on radiation protection being at a level, close but lower than of the health admitted norms.

In terms of basic physical characteristics, the ash can be assimilated to a natural sand aggregate of granular type, except for bulk density characterized by lower values.

The results show that vitrified ceramics can be developed from coal ash and provide the best conditions to obtain products with desirable properties suitable for construction sector.

Acknowledgements

The present research has been carried out with the financial support given through LIFE10 ENV/RO/729 Project.

References


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**Annex**

![Image](image_url)

**Fig. 1.** (a) coal ash dump of ECT; (b) dry ash samples

**Table 1. Physical characteristics of the average ash samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Moisture (%)</th>
<th>Grain size composition (%)</th>
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<td></td>
<td>4</td>
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<tr>
<td>A</td>
<td>25.47</td>
<td>1.84</td>
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<tr>
<td>B</td>
<td>26.78</td>
<td>1.43</td>
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<tr>
<td>C</td>
<td>25.83</td>
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<tr>
<td>D</td>
<td>25.88</td>
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<td>0.62</td>
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<td>ABCD</td>
<td>25.99</td>
<td>1.51</td>
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Fig. 2. Grain size distribution of ash average samples

Table 2. Chemical composition of the average ash samples

<table>
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<tr>
<th>Sample</th>
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<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>MgO</th>
<th>CaO</th>
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<th>K$_2$O</th>
<th>TiO$_2$</th>
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<th>SO$_3$</th>
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<td>0.08</td>
<td>0.21</td>
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<td>0.08</td>
<td>0.19</td>
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<td>0.21</td>
<td>4.6</td>
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<tr>
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<td>0.07</td>
<td>0.20</td>
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<td>8.9</td>
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<tr>
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<td>1.44</td>
<td>0.72</td>
<td>0.22</td>
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<td>9.09</td>
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Table 3. Mineralogical crystalline phases identified by XRD on coal ash sample

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<th>Sample</th>
<th>Mineralogical crystalline phases identified by XRD</th>
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<tr>
<td>A</td>
<td>Quartz - SiO$_2$ Anorthit – CaAl$_2$(SiO$_4$)$_2$</td>
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<tr>
<td></td>
<td>Hematite – Fe$_2$O$_3$</td>
</tr>
<tr>
<td>B</td>
<td>Quartz - SiO$_2$ Anorthit – CaAl$_2$(SiO$_4$)$_2$</td>
</tr>
<tr>
<td></td>
<td>Hematite – Fe$_2$O$_3$</td>
</tr>
<tr>
<td>C</td>
<td>Quartz - SiO$_2$ Anorthit – CaAl$_2$(SiO$_4$)$_2$</td>
</tr>
<tr>
<td></td>
<td>Hematite – Fe$_2$O$_3$</td>
</tr>
<tr>
<td>D</td>
<td>Quartz - SiO$_2$ Anorthit – CaAl$_2$(SiO$_4$)$_2$</td>
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<tr>
<td></td>
<td>Hematite – Fe$_2$O$_3$</td>
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</tbody>
</table>
Fig. 3. XRD pattern of ash sample (A)

Fig. 4. Location of the ashes oxide average composition in the ternary system CaO - Al₂O₃ - SiO₂

Fig. 5. TG/DTA diagram for coal ash (average sample A)
Fig. 6. **Patterns** of geometry change of coal ash specimen (with average composition)